Gas hydrate distributions in sediments of pockmarks from the Nigerian Margin - Results and interpretation from shallow drilling

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Abstract :

A joint research expedition between the French IFREMER and the German MARUM was conducted in 2011 using the R/V Pourquoi pas? to study gas hydrate distributions in a pockmark field (1141 – 1199 meters below sea surface) at the continental margin of Nigeria. The sea floor drill rig MeBo of MARUM was used to recover sediments as deep as 56.74 meters below seafloor. The presence of gas hydrates in specific core sections was deduced from temperature anomalies recorded during continuous records of infrared thermal scanning and anomalies in pore water chloride concentrations. In situ sediment temperature measurements showed elevated geothermal gradients of up to 258 °C/km in the center of the so-called pockmark A which is up to 4.6 times higher than that in the background sediment (72 °C/km). The gas hydrate distribution and thermal regime in the pockmark are largely controlled by the intensity, periodicity and direction of fluid flow. The joint interaction between fluid flow, gas hydrate formation and dissolution, and the thermal regime governs pockmark formation and evolution on the Nigerian continental margin.

Keywords : gas hydrate, pockmark, chloride profile, infrared thermal imaging, fluid flow, Nigerian continental margin, MeBo drill rig
1. Introduction

Pockmarks are circular to elongated seafloor depressions which are often associated with fluid flow from the subsurface (Judd and Hovland, 2007). Submarine pockmarks with various sizes, shapes and state of activity have been widely discovered at different water depths (e.g. Bünz et al., 2003; Chen et al., 2010; Dondurur et al., 2011; Pilcher and Argent, 2007; Pinet et al., 2010; Sahling et al., 2008; Sun et al., 2011; Ussler et al., 2003). In addition, buried paleo-pockmarks found during seismic investigations were proposed to be associated with periodic fluid flow activity in the past (Andresen et al., 2008).

Depending on the local geological conditions, several mechanisms have been suggested to explain the process of pockmark formation. Researchers tend to agree that pockmarks are directly or indirectly caused by upward fluid flow from the deep subsurface, through moderate to violent processes (Chand et al., 2012; Gay et al., 2006a; Gay et al., 2006b; Hartwig et al., 2012; Moss et al., 2012; Paull et al., 2008; Riboulot et al., 2013; Rise et al., 1999). In particular on continental margins, methane oversaturated in upward migrating fluids reacts under high pressure and low temperature in shallow sediment to form solid gas hydrate (Matsumoto et al., 2011; Sloan and Koh, 2007). The structural properties of gas hydrate, like its fabric, and the hydrate saturations in the sediment, are largely controlled by the intensity and distribution of fluid flow and by the sediment properties, including permeability and strength (Abegg et al., 2007). Moreover, fluid migration patterns are changed by pore space blocking caused by gas hydrate formation (Bangs et al., 2011; Riedel et al., 2006). The interaction between fluid flow, gas hydrates and host sediment increases the complexity of the pockmark system and is of significant
importance when studying the formation and evolution of deep-water pockmark located in the gas hydrate stability zone (GHSZ).

Sultan et al. (2010) proposed an initial model for the formation of individual pockmarks on the Nigerian continental margin. Based on gas hydrate findings in shallow sediments and numerical modeling of the dynamic response of the gas hydrate to changes in gas concentrations underneath the gas hydrate occurrence zone (GHOZ), gas hydrate formation and dissolution was suggested to be the major control for the evolution of these pockmarks. In order to gain further insight, a joint research expedition (Guineco-MeBo) between the French IFREMER and the German MARUM with the R/V *Pourquoi pas?* and the portable sea floor drill-rig MeBo was conducted in 2011. The major objective of the expedition was to reveal gas hydrate distributions in even deeper sediments, which eluded sampling with common sampling techniques (e.g., long piston cores) before.

In this study, gas hydrate distributions in sediments of selected pockmarks were determined using infrared (IR) thermal scanning of core liners and pore water chloride analysis. Furthermore, the impact of fluid flow and gas hydrate formation/dissolution on controlling the geothermal regime and evolution of the pockmarks is discussed.

2. Geological settings

Our study area is a pockmark field located within the Gulf of Guinea on the continental margin offshore Nigeria (Fig. 1). This continental margin is undergoing slow deformation by gravity tectonism that initiated in response to both, rapid seaward progradation and loading huge amount of sediment (Damuth, 1994). Damuth (1994) distinguished this area
into three subareas based on the structural styles: 1) an upper extensional zone, 2) an intermediate translational zone, and 3) a lower compressional zone. The pockmark field studied in this paper is located in the translational zone which is characterized by diapirs underneath. Examples of seismic recordings of shale diapirs in this area can be found in Damuth (1994) and Cohen and McClay (1996).

The Nigerian continental margin is an active fluid flux area as indicated from various seafloor features, such as pockmarks, mud volcanoes, gas hydrates and carbonate concretions (Bayon et al., 2007; Brooks et al., 2000; Graue, 2000; Hovland et al., 1997). Formation of such authigenic carbonates is typically attributed to the anaerobic methane oxidation (AOM; Ritger 1987). Pronounced bottom simulating reflectors (BSR), demonstrating the boundary between the base of the GHSZ and free gas underneath, were reported (Cunningham and Lindholm, 2000). Such BSRs indicate the presence of gas hydrates related to high methane flux towards shallow sediments caused by fluid migration (Hovland et al., 1997). In addition, gas chimneys found in the subsurface were proposed to serve as pathways for fast hydrocarbon migration between reservoirs and the seafloor (Heggland, 2003).

The pockmark field, comprising the pockmarks A and C studied herein, lies at water depths between 1141 and 1199 m. Pockmark A (Fig. 1C) is a slightly NE-SW elongated seafloor feature with a hummocky topography in the center. The hummocky area corresponds to high multibeam backscatter (George and Cauquil, 2007) which may indicate the occurrence of shallow gas hydrates, free gas and/or authigenic carbonates (Carson et al., 1994). Pockmark C (Fig. 1D) is a pockmark cluster composed of at least
three pockmarks (C1 – C3). Shallow gas hydrates were found widely in this pockmark field which might contribute to the formation of the pockmarks (Sultan et al., 2010). Authigenic carbonates were also recovered from different depths in these pockmarks (Sultan et al., 2010).

3. Material and methods

3.1 MeBo drilling

The mobile drilling system MeBo (Freudenthal and Wefer, 2013) was deployed from the R/V ‘Pourquoi pas?’ to drill 12 cores of up to 56.74 m in length in the pockmark field between 1141 and 1199 m water depth (Fig. 1; Table 1). Seven drill sites were located in and around pockmark A (Fig. 1C), with five sites in the central part (GMMB06, 07, 08, 10 and 11) and two in the periphery (GMMB03 and 12). Two drill sites (GMMB01 and 02) were located outside (NW) pockmark A. Further three drill sites (Fig. 1D) were located in pockmark C1 (GMMB04), pockmark C2 (GMMB05), and SE of pockmark C2 (GMMB09), respectively.

3.2 Infrared thermal imaging of MeBo cores

Infrared (IR) temperature profiles of the 2.52 m-long MeBo core liners were obtained for 10 drill sites in order to document the gas hydrate distribution in the MeBo cores. Images for GMMB10 were not interpreted due to their low quality. The core liners were removed from the core barrels immediately after recovery on deck. After a quick cleaning of the liner surfaces, pictures were taken with an IR camera (ThermaCam SC 640 camera, FLIR Systems) for documenting temperature variations. The temperature measurements of the
IR system ranged from $-40 \degree C$ to $+120 \degree C$ and the precision of the camera was $0.1 \degree C$ at $30 \degree C$ with the accuracy of $\pm 2 \degree C$. Each thermal scan covered approximately 60 cm depth range of the core. Five to six pictures including a spatial overlap of about 10 cm were taken from each liner in less than one minute.

For an individual drilling station, all IR images were combined in one figure to display the temperature distribution for the entire core surface. The raw data were converted and exported as bitmap format using the ThermaCAM™ Researcher Professional software. The bitmap files were processed using commercially available graphical software. All IR images were merged consecutively, considering distinct hot or cold spots as reference points. Temperatures along the central axis of the cores were extracted from the IR images to obtain temperature logs (Fig. 2). Surface temperatures of core liners containing sediment devoid of gas hydrates were considered as background temperature. At each drilling station, background temperatures varied slightly (ca. $1–2 \degree C$) between individual liners due to different in situ sediment temperatures and/or slightly different times required for individual liner handling (equilibration with ambient temperature of $\approx 30 \degree C$ on ship’s deck). Thus, the specific background temperature was assigned to each core liner individually.

The difference between liner surface temperature and background temperature ($\Delta T$) was calculated to interpret the content of the cores. In order to obtain a better visualization and to minimize the artifacts for further analysis, only anomalies with $\Delta T >+1 \degree C$ were considered as voids in the liner and $\Delta T <–2 \degree C$ were considered to represent hydrate-bearing sediment, as hydrate dissociation is an endothermic process.
3.3 Pore water chloride and sulfate analysis

Pore water was extracted using Rhizon samplers (Seeberg-Elverfeldt et al., 2005), which consists of a thin tube made up with hydrophilic porous polymer with pore diameters of approximate 0.2 µm. The Rhizon samplers were pushed into the sediment through holes drilled through the plastic liners. 10 or 20 ml plastic syringes were connected to the sampler to create a vacuum and collect the pore water. Extracted pore water was split, prepared for various analyses, and stored in the refrigerator or reefer. Sulfate and chloride concentrations were measured on-board by using ion chromatography (861 Advanced Compact IC, 837 IC Eluent Degasser, and Advanced Sample Processor by Metrohm).

For several MeBo stations, seawater-derived sulfate in detectable concentrations was not only found in near-surface sediments but also in deeper layers. This was unexpected because sulfate is typically depleted below the sulfate-methane interface (SMI) due to AOM. Moreover, since measured sulfate concentrations below the SMI scattered considerably, we assumed that the presence of sulfate in these core sections were artifacts caused during the core drilling/handling procedure. Therefore, concentrations of chloride were re-calculated assuming the absence of sulfate below the SMI. This procedure caused changes in absolute chloride concentrations of <20% but affected trends in chloride profiles insignificantly.

3.4 In situ temperature measurements

In-situ temperature measurements were conducted in pockmark A using autonomous miniaturized temperature loggers (MTLs) from ANTARES Datensystem GmbH
(Germany), which have already been used successfully during previous studies (Römer et al., 2012; Feseker et al., 2009; Pape et al., 2011). Five temperature sensors were mounted on outriggers attached to the cutting barrel of a 6 m-long gravity corer according to Feseker et al. (2009). Distances between the loggers were 100 cm and the logging time interval was set to 5 sec. For each deployment, the gravity corer was held 50 meters above the seafloor for three to four minutes to measure the water temperature for calibration purposes of each MTL. Based on these measurements the standard deviation of the five loggers was calculated to be smaller than 0.008 °C (Table 2). At each station, the loggers were left in the sediment for about 15 minutes (Fig. 5) after penetration of the gravity corer to adjust to the sediment temperature. The absolute penetration depths could be estimated from mud smear on the gravity corers or on the cable. By using linear regression individual temperatures recorded with the MTLs and assumed penetration depths were used to calculate the site-specific geothermal gradients.

4. Results

MeBo was deployed 12 times in total during the entire cruise. Depending on the lithology as well as on gas and gas hydrate contents, the recovery of the drill cores ranged between 60% and 94% with a mean of 81%. The cores comprised homogenous hemipelagic dark greyish clay with sporadic authigenic carbonate concretions. Distinct depth-changes or lateral variations of sediment grain sizes were not observed. Sediments with elevated water content, which was attributed to ex situ gas hydrate dissociation, were observed at different depths without regularity. No relation between gas hydrate distributions and sediment grain sizes became obvious.
4.1 Infrared thermal imaging

Infrared (IR) temperature profiles of core liners were established for most of the drill sites. The only exceptions were station GMMB01 and GMMB02 outside of pockmark A since indications for the presence of gas hydrates in sediments within the penetration depth (53.3 meters below seafloor (mbsf)) at these drill sites were missing in seismic profiles (Sultan et al., 2010). The assumption of the gas hydrates absence in these sediments was confirmed by the subsequent pore water chloride profiling (see chapter 4.2).

Comparison of IR images with lithological core descriptions and high-resolution core photographs showed that thermal regimes of the MeBo cores were mainly determined by the core contents. This is exemplary shown for core GMMB06 (Fig. 2). Since the in situ temperature of sediment (~4.5 °C) was significantly lower than that of the upper water column (up to ~28 °C) and the atmosphere (~30 °C), the cores were continuously warmed up during the core recovery and handling on deck. Liners filled with sediment exhibited intermediate temperatures of 23–25 °C (Fig. 2A), depending mainly on the duration they were exposed to the water column and air before being imaged. These temperatures were considered as background.

Cores containing dissociating gas hydrates yielded prominent cold anomalies since hydrate dissociation happening during core recovery and handling is an endothermic process. The temperature decrease is mainly influenced by the volume of gas hydrate pieces and the decomposition speed. The extent of cold temperature zones reflects in many ways the fabric of gas hydrates in the liners. Disseminated gas hydrates are prone to dissociation in a relatively short time. After a very short time of dissociation-induced
cooling which occurs relatively homogenously throughout a respective core section. Because of the relatively small amount of water released during decomposition of disseminated hydrates, residual sediments often show a moussy fabric (Weinberger et al., 2005) and exhibit moderate negative $\Delta T$ of $-3 \, ^\circ C$ to $-4 \, ^\circ C$ (Fig. 2B). In contrast, nodular gas hydrates, massive hydrate layers or hydrate-filled fractures usually occurring in distinct intervals reveal stronger negative $\Delta T$ of up to $-10 \, ^\circ C$ (Fig. 2C). Decomposition of such hydrate fabrics principally takes much longer time than that of disseminated hydrates because of both, their comparably smaller surface area and the resulting higher efficiency of the self-preservation effect (Sloan and Koh, 2007). During decomposition of nodular/massive hydrates the residual sediment might become very soupy because of the high volume of hydrate water released.

Voids or gaps defined as empty intervals in the liners are often due to gas expansion. They are typically represented by positive $\Delta T$ of $+2 \, ^\circ C$ to $+4 \, ^\circ C$ (Fig. 2A and 2C) because the effective heat capacity of the gas/air filled liner strongly differs from that of sediments and the temperature gets into equilibrium with the ambient air rapidly. Voids within gas hydrate-bearing sediments (Fig. 2C) are generated by gas expansion likely caused by gas release from hydrate dissociation. In contrast, voids within non-hydrate sediment (Fig. 2A), are likely caused by methane release from the dissolved phase due to the pressure drop during core recovery. High-temperature patches with absolute temperatures of more than $30 \, ^\circ C$ as shown in Fig. 2A are core handling artifacts.

Since the IR thermal patterns of the cores are mainly controlled by their contents, they were classified into four groups (Fig. 3).
IR-temperature pattern 1: Sediment without gas hydrates

Homogenous hemipelagic sediment was represented by moderate temperatures of 23–25 °C (Fig. 2A). It was present in the top few meters of all cores (from 1.2 mbsf in GMMB11 to 38.5 mbsf in GMMB09). It also occurred at the bottom of some cores below the gas hydrate occurrence zone (GHOZ), including GMMB03, GMMB05, GMMB08 and GMMB12 (Fig. 3).

IR-temperature pattern 2: Sediment with gas hydrate

Gas hydrate-bearing sediments showed relatively low temperatures (less than ~22 °C) of the liner surface (Fig. 2B and 2C). Associated voids represented by positive \( \Delta T \) were also observed. Since the voids are mainly caused by gas expansion during hydrate dissociation, which pushes the sediments apart, void intervals were included in pattern 2 as well.

IR-temperature pattern 3: High gas concentration

This temperature pattern was defined for core sections with relative moderate temperature between 23 and 25 °C, separated by distinct voids represented by slightly warmer temperatures of ~27 °C. In some gas hydrate-free sediment intervals, cm-scaled voids appeared in a dense pattern and revealed positive \( \Delta T \) in the IR images (e.g. 30.0-38.5 mbsf in core GMMB09; Fig. 3). Formation of voids is attributed to the expansion of methane gas excluded from the dissolved phase due to depressurization.

IR-temperature pattern 4: Intervals of unidentified liner content
Large unfilled sections adjacent to gas hydrate-bearing sediment were occasionally observed, for example in GMMB07 and GMMB11 (Fig. 3). However, it remained unclear whether gas hydrates were present in these sections prior to IR imaging. Thus, we defined these core sections as intervals of unidentified liner content.

4.2 Pore water chloride concentrations

Chloride concentrations in pore waters of 12 MeBo cores were measured to study vertical gas hydrate distributions and to compare the results with those obtained by IR thermal scanning (Fig. 3). Chloride concentrations in bottom waters were around 550 mM and were also measured in near-surface sediments. With increasing depth, Cl\(^{-}\) concentrations showed a slightly decreasing trend in some cores such as GMMB08 and GMMB03. By considering Cl\(^{-}\) = 550 mM as background, discrete positive and negative concentration anomalies were identified in the cores. Negative anomalies, with minimum concentrations of 213.1 mM at 38.83 mbsf in core GMMB09, were found widely distributed in gas hydrate-bearing sediments. These were caused by the dilution of pore water by Cl\(^{-}\)-free water which is released by hydrate dissociation during core recovery (Torres et al., 2004a; Tréhu et al., 2004). Discrete positive Cl\(^{-}\) anomalies, of up to 1059.7 mM, in contrast are proposed to be associated with fast hydrate formation. During formation of gas hydrates ions are excluded from the hydrate lattice, which results in an increases in pore water chloride concentrations (Torres et al., 2011; Torres et al., 2004b). In previous studies it was observed that for chloride back diffusion to background concentrations takes a comparably long time (Haeckel et al., 2004). Therefore, positive anomalies existing in situ can still be detected by conventional pore water analysis in case
quick sampling prevents pore water dilution by fresh water from dissociating hydrates. Since the pore water samples were taken immediately before the massive hydrates were totally decomposed, the elevated chloride concentrations are a proxy for relatively recent hydrate formation in sediments of the pockmarks.

4.3 Regional and depth variations in gas hydrate distributions

Both proxies, IR imaging and pore water chloride concentration profiling, revealed similar gas hydrate down core distributions and only for some small intervals results from both methods did not correlate (Table 1). Hydrates in pockmark A were present in the central part at much shallower depth compared to the periphery (Fig. 3, Table 1). Temperature anomalies captured by the IR images indicated that the top of the GHOZ in the central part (GMMB06, GMMB07, GMMB08 and GMMB11) ranges from 2.3 mbsf (GMMB08) to 6.5 mbsf (GMMB11), whereas chloride anomalies revealed hydrate presence from 1.2 mbsf (GMMB11) to 4.4 mbsf (GMMB10). Peripheral cores (GMMB03 and GMMB12) showed down core gas hydrate presence from 6.9 to 7.6 mbsf by using IR imaging and 6.1 to 6.7 mbsf based on chloride anomalies (Fig. 3). These data sets substantiate a very shallow top of the GHOZ in the pockmark center which deepens towards its rim as already suggested by Sultan (2010). In core GMMB08, taken in the NW central part of pockmark A, the down core gas hydrate distribution was indicated by IR imaging down to 26.4 mbsf and by the chloride proxy down to 24.1 mbsf. In cores GMMB03 and GMMB12 taken at the periphery of pockmark A, gas hydrate occurrences were present from about 7 mbsf down to about 17 mbsf.
In pockmarks C1 and C2, the top of the GHOZ was determined to be positioned between 5.9 mbsf and 10.3 mbsf using IR imaging proxy, and 5.3 mbsf and 8.5 mbsf using chloride anomalies (Fig. 3). Outside pockmark C2, core GMMB09 showed the deepest gas hydrate occurrence of all MeBo cores from about 38.5 mbsf down to its maximum penetration depth of 43.6 mbsf (Fig. 3).

4.4 In situ sediment temperatures

In situ temperature measurements conducted at ten stations in pockmark A using MTLs showed slight variations in water temperatures ranging between 4.45 and 4.53 °C (Fig. 4, Table 2). For the in situ sediment temperature measurements most geothermal gradients showed linear or sub-linear slopes. The thermal gradient established at station GMGCT22, which was performed outside pockmark A and is considered as reference station, was about 72 °C/km. Similar thermal gradients ranging between 51 and 79 °C/km were determined for four other stations (GMGCT23, 24, 41 and 49). At a cluster of five stations performed in the hummocky area elevated geothermal gradients were observed. Slightly elevated gradients of 112 and 119 °C/km were measured at stations GMGCT46 and -47, respectively. At stations GMGCT44, -45 and -40, the gradients were 198 and 330 °C/km, which is 2.8 and 4.6 times higher than the gradient at the background station, respectively. At station GMGCT40 a considerably elevated temperature deviating from the general trend established by the other MTLs was measured with TL-2 at a sediment depth of about 2 mbsf (Fig. 4).
5. Discussion

5.1 Thermal regime of pockmark A

The geothermal gradient in the central part of pockmark A was significantly higher than the local background gradient (Fig. 4). Elevated temperatures in marine sediments caused by fluid flow have been widely reported from active mud volcanoes (e.g. Feseker et al., 2008; 2009a;b; Foucher et al., 2010) and other marine seep types (Römer et al., 2012). At pockmark A studied herein indications for mud flow activities such as mud breccia (Kopf, 2002) have not been found. However, free gas ebullition observed above the central part of pockmark A during the expedition (for location see Sultan et al., 2014) proves fluid upward migration at this structure. Thus, the temperature elevation in shallow sediment is likely caused by fluid advection.

It is worth noting that none of our measured geothermal profiles is strictly linear. We assume that besides the influence from heat convection induced by fluid flow, precipitation of gas hydrates in pore space contributes partially to this phenomenon. Several physical bulk sediment properties (i.e. thermal conductivity, heat capacity, density) are altered by gas hydrate precipitation in the pore space. In particular, gas hydrate formation is an exothermic reaction and heat is released when hydrate crystallizes (Sloan and Koh, 2007; Waite et al., 2007). Waite et al. (2007) pointed out that the thermal diffusivity of sediment with 60% porosity and 40% gas hydrate saturation increases by 20% compared to that of non-hydrate-bearing sediment. The gas hydrate saturation in the studied pockmarks is not quantified yet. Nevertheless, we conservatively estimate that gas hydrate saturations in specific sediment depths do not exceed 40% and that deviations...
of absolute temperatures caused by hydrates are <20% with respect to a hypothetical linear thermal gradient throughout the sediment.

At station GMGCT40 (Fig. 4) an exceptionally high temperature was measured with TL-2 if compared to the other temperature loggers mounted below and above. This phenomenon was also observed at a high-flux seep area in the Black Sea (Römer et al., 2012). Fig. 5 shows the continuous temperature change with time recorded with the loggers during stations GMGCT40 and 41 when the corer has not been lifted out of the water. It becomes obvious that at station GMGCT40 the absolute temperature measured with TL-2 was generally highest and that the temperature slope reversed after a while. Temperatures determined with TL-1, -3, and -4 were lower and reached equilibrium in contrast to that of TL-2. During station GMGCT41 absolute temperatures changed according to the expected order which corresponded to the arrangement of loggers at the gravity corer.

The temperature difference between TL-1 and TL-2 is 0.127 °C which is two orders of magnitude higher than the logger accuracy (see Table 2). Thus, we conclude that the temperature measured with TL-2 was neither noise nor caused by wrong operation. However, if we ignore the temperature measured with TL-2, temperatures determined with the other three loggers show a linear regression with a slope similar to those of GMGCT44 (198°C/km) and GMGCT45 (258°C/km) (see Fig. 4).

The exceptionally high temperature recorded at about 2 mbsf at station GMGCT40 cannot be explained by vertical fluid advection and/or sediment thermal properties changed by hydrate formation. It is obvious that additional heat was generated at the depth
between TL-1 and TL-3. In a 3D complex pockmark, spatially restricted temperature
elevations might be caused by lateral heat advection from fluid flow along fractures or
fast gas hydrate formation. Gas hydrate formation and dissociation are exothermic and
endothermic processes, respectively, which subsequently change the thermal regime of
pockmarks (Chen and Cathles, 2005). During the cruise, gas hydrate with bubble fabric,
which is an indication of fast gas hydrate crystallization from methane bubbles
(Bohrmann et al., 1998), was sampled with gravity cores. Since gas hydrate occurs
widely in the center of pockmark A, its crystallization could release significant amounts
of heat (Chen and Cathles, 2005). Although we did not further investigate the amount of
freshly formed hydrate required to induce the relative temperature increase observed, we
speculate that TL-2 might have intersected with a fracture in which either gas hydrate
precipitated rapidly and/or fluid flowed happened facilitating lateral heat convection.

Because gas hydrates are sensitive to temperature variations (e.g. Feseker et al., 2009b;
Pape et al., 2011; Römer et al., 2012; Berndt et al., 2014) thermal variations in the
sediment impact gas hydrate distributions. At active seeps, temperature elevation in
shallow sediments due to fluid advection lift the base of the GHSZ (e.g. Ginsburg et al.,
1999; Römer et al., 2012). Considering the maximum (258 °C/km) and minimum
(72 °C/km) geothermal gradients determined in this study (Table 2), the base of the
GHSZ under pockmark A should be situated between 35 mbsf and 130 mbsf, respectively
(Fig. 6). Since high thermal gradients were detected only in a restricted area NW of the
geometrical center of the pockmark, we assume that distinct temperature elevations
caused by fluid advection influence the GHSZ only on a small scale. In the water column,
the top of the GHSZ is estimated to be at 587 mbsl which is consistent with the maximum height of gas flares observed above pockmark A during the cruise (Sultan et al., 2014).

### 5.2 Gas hydrate and fluid flow

Results from IR scanning and pore water chloride concentration analysis of the MeBo cores as well as recoveries substantiate gas hydrate presence in shallow (meters to tens of meters depth) sediments of the three studied pockmarks. It was shown that shallow gas hydrates at active marine seeps primarily form from free gas (Haeckel et al., 2004; Römer et al., 2012; Sahling et al., 2008; Torres et al., 2004b; Wallmann et al., 2006). Gas flares observed above pockmark A during the survey in 2011 are direct evidence of gas flow through the sediment (Sultan et al., 2014). Therefore, we assume that gas hydrates in the studied pockmarks are mainly formed from the free gas phase. Free gas captured in pockets within the GHOZ might contribute to the high amplitude reflectors observed in seismic records from that area (Figs. 7). In particular, at station GMMB04 in pockmark C1 showed vigorous gas expulsion during drilling at ~18 mbsf, which corresponds to distinct high amplitude reflectors (Fig. 7B) (Sultan et al., 2014).

Free gas can migrate along fractures and gas hydrate can precipitate along fracture walls (Torres et al., 2004b; Flemings et al., 2003) where fluid pressure and crystallization forces are less than the effective overburden stress. In case free methane-rich gas migrates upward into shallow sediment, where fluid pressure and crystallization force exceed the effective overburden stress, it spreads out in the pore space and reacts with water, forming gas hydrate (Torres et al., 2004b). This assumption is supported by our observation of gas hydrates present within the upper ~30m (Figs. 2, 3, 7). Because the
maximum depth of the GHSZ at pockmark A is situated at around 130 mbsf (geothermal gradient: 72 °C/km; Table 2; Fig. 6), we might assume that gas hydrate also forms at greater depth.

However, gas flow in a seep system is not under steady state (Bangs et al., 2011; Chand et al., 2012; Gay et al., 2006b; Greinert et al., 2006) and pressure drop in deep gas reservoirs (Bangs et al., 2011) and/or sealing of pathways by gas hydrate formation (Riedel et al., 2006) might result in a decrease, or even cease of gas flow. Thus, although no gas flares were recognized at pockmark C1 and C2 during this expedition, gas hydrates in these two pockmarks likely formed from active gas flow in the recent past.

Upward gas migration stimulates the anaerobic methane oxidation (AOM) mediated by methanotrophic archaea and sulfate reducing bacteria in near-surface sediments (Hoehler et al., 1994; Boetius et al., 2000), and the resulting end products, such as hydrogen sulfide, nourish a chemosynthesis-based ecosystem (Sahling et al., 2008). During our expedition living vesicomyid clams, which rely on sulfide oxidation, were recovered from the seafloor in the studied area, indicating a living chemosynthetic ecosystem. However, as mentioned above, gas flow at a seep system is a transient process. Bangs et al. (2011) pointed out that methane gas flow for a vent at Southern Hydrate Ridge has undergone significant reduction or complete interruption within just a few years, whereas the associated ecosystem has persisted for thousands of years. This observation raises the question, how the chemosynthesis-based species survive during periods of reduced gas flow. In a gas hydrate setting methane diffuses continuously from the shallow gas hydrate reservoir towards the methane-depleted sea water and sustains AOM. This is consistent
with the assumption of Sultan et al. (2010) that many gas hydrate reservoirs in the study area are currently undergoing dissolution due to insufficient methane supply from greater depth. Similar conclusions of chemosynthetic-based macrofauna presumably relying on continuous methane supply from decomposing hydrates were already proposed for seep systems in other regions (e.g., Paull et al., 1995; Pape et al., 2014). Thus, we propose that gas hydrate reservoirs in shallow sediments serve as a capacitor (see e.g. Dickens, 2003), as they form rapidly during a high gas-flow phase, and sustain the seep ecosystem by slow methane diffusion when the gas flow from below is reduced.

5.3 Pockmark formation

It was initially proposed by Sultan et al. (2010) that gas hydrate dissolution caused by insufficient gas supply is the controlling factor for pockmark formation and evolution in the study area. New field data suggested that pockmark formation is not only controlled by slow gas hydrate dissolution but also by rapid hydrate formation (Sultan et al., 2014). Based on the data obtained from the MeBo cores in this study, an improved but simple model comprising five stages is suggested for the evolution of the pockmarks (Fig. 8) in the studied area.

Stage A: Gas migrates from a deep source. Within the GHSZ, when the hydrate crystallization force overcomes the burden of the overlying sediment, gas hydrate starts precipitating in the shallow sediment. Gas hydrate growth decreases the pore space availability and sediment permeability and clogs the pathways of fluid flow, which subsequently decreases or even ceases the fluid flow in uppermost sediments. During this
stage, there is neither a distinct morphological change on the seafloor nor gas emission into the water column.

Stage B: In case of reduced gas flow to shallow sediments, sulfate can penetrate to greater depths, which leads to a downward shift of the SMI (see e.g. Borowski et al., 1996). Methane in the shallow sediment is likely depleted due to diffusion and AOM. As a result, gas hydrates dissolve from the top of the GHOZ (see Sultan et al., 2010). Subsequently, the overlying sediment is deformed due to the volume loss below and a seafloor depression is created. This stage might explain the ~2 m depression observed for pockmark C2 (Figs. 1 and 7).

Stage C: Once the fluid flow is re-intensified, methane and shallow hydrate repeat the same procedure as described in Stage A. When pore pressure surpasses a threshold value, fractures are generated in the overlying sediment at the pockmark center (e.g. observed in pockmark A, Fig. 7) which might serve as pathways for free gas to migrate to the seafloor. Since these fractures form within the GHSZ, gas hydrates might accumulate along the fracture walls which efficiently prevents the contact between pore water and gases. Fast gas hydrate formation will significantly increase the salinity of the surrounding pore water due to ion exclusion and the resulting brine might locally prevent gas hydrate formation (Ussler & Paull, 1995; Torres et al., 2011). Massive gas hydrate accumulating in the shallow sediment expands the mass volume and creates convex-shaped elevations as well as a rough seafloor, like observed close to the center of pockmark A (Fig. 1). This can explain the cones and hummocky structure at the centers of pockmarks A and C1 (Fig. 7).
Stage D: In case the methane flux is redirected towards shallow sediments in the vicinity of the initial pockmark, a new pockmark might be created and might repeat stages A-C.

Stage E: The complexity and size of a pockmark might increase significantly in case more and more new pockmarks morphologically combine (Marcon et al., 2014). It might be assumed that pockmark C1, which exhibits a roughly NE-SW seafloor expression and complex seafloor morphology, is composed of several small pockmarks at different stages.

6. Conclusion

Gas hydrate distributions in the sediment of three pockmarks on the Nigerian continental margin were investigated by applying infrared (IR) thermal imaging and pore water chloride and sulfate concentration measurements on cores recovered with the portable MeBo drill rig. In addition, ten in situ sediment temperature measurements were performed to study the geothermal regime of the individual pockmark A. Based on the temperature and chloride anomalies, the following conclusions are drawn:

1. Negative temperature anomalies detected by IR thermal scanning as well as positive and negative chloride anomalies in pore waters indicated the presence of gas hydrate in shallow pockmark sediments. Distributions of gas hydrate-bearing sediments as inferred from both methods match each other.

2. Geothermal gradients up to 5 times higher in the center of pockmark A than the background were interpreted to result from enhanced heat advection caused in the course of fluid flow and potentially also to fast growth of gas hydrates.
3. Recent hydrate formation is inferred from positive chloride anomalies.

4. Gas hydrate precipitation and dissolution caused by the variation of fluid flow exert significant impact on the formation and evolution of pockmarks on the Nigerian continental margin.
Acknowledgement

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Figure captions:

Figure 1: (A): Location of the pockmark field at the Nigerian continental margin. (B): Overview of the studied pockmark field. (C) and (D): MeBo drill sites (GMMB) in pockmarks A and C (C1 and C2), respectively. Numbers refer to individual MeBo station codes (i.e. No. 01 = station GMMB01, for example) Track lines of SYSIF seismic profiles SY03-THR-Pr01 and SY01-HR-Pr02 as well as the shot points are shown. For exact positions refer to Sultan et al. (2014).

Figure 2: Combined illustration of core photographs (left) and IR images (right) of the 6.6 m-long MeBo drill core GMMB06. Representative intervals of the core (A, B and C) are shown in detail (right part of the figure). (A): normal hemi-pelagic sediment (upper part) and voids (lower part), which in the IR images correspond to the background temperature (orange) and high temperature (yellow), respectively. The bright spot (white) is an artifact generated during the core handling. (B): Moussy sediment with cracks, which in the IR image shows three cold temperature zones (light purple) caused by the dissociation of disseminated gas hydrates. (C): Soupy and fluidized sediments. The cold temperature interval below 5.70 mbsf contained gas hydrates including a nodular gas hydrate between 5.80 and 5.85 mbsf represented by an extremely cold spot (dark purple to black). GH = gas hydrate

Figure 3: IR temperatures and pore water chloride concentration profiles of MeBo cores. Four data sets are shown for most drill sites: IR image colors, IR temperature profiles, interpreted gas hydrate distributions, and chloride profiles. The color bar of the IR images is consistent with Fig. 2 and white intervals indicate gaps. Temperature profiles show the differences between the measured temperature and background temperatures of core liners, expressed as $\Delta T$. Positive $\Delta T$ values correlate with voids in the cores and negative $\Delta T$ values represent decomposing gas hydrates. The approximate down-core gas hydrate presence interpreted from IR images is
indicated by colored bars and indications for depth below seafloor (mbsf). Depths of gas hydrate-bearing intervals as inferred from chloride anomalies are highlighted in blue shading. Note that the chloride data of the upper 12.7 mbsf at station GMB09 were derived from a piston core (GMCS10) taken at the same position.

Figure 4: A: Position of sites chosen for temperature measurements in pockmark A. B: *In situ* sediment temperature measurements. Temperature gradients were classified into two clusters: (1) background gradients (around 72 °C/km) highlighted by the dark grey background, and (2) high gradients caused by fluid advection without background color.

Figure 5: Temperature change with time at stations GMGCT40 and GMGCT41. TL-1 to TL-5 represents the temperature sensors attached to the corer from base to top. Remarkably, the temperature measured with TL-2 at station GMGCT40 increased continuously after penetration and was higher than that of TL-1, which penetrated deeper into the sediment. Note that TL-5 had no contact with sediment and, therefore, measured bottom water temperature.

Figure 6: Phase diagram calculated for structure I gas hydrates with the HWHYD software (Masoudi and Tohidi, 2005) and using salinities and pure methane because methane concentration of hydrate-bound gas is higher than 99.9% (unpublished data). A CTD record was used to show the water column temperature profile. 72 °C/km (GMGCT22) was used as the local background geothermal gradient outside the pockmarks, while 258 °C/km (GMGCT45) was measured close to a site at pockmark center which showed seafloor gas emission (see Sultan et al., 2014). The subsurface part (dash blue rectangle) of the diagram is enlarged in the right part of the figure.

Figure 7: SYSIF seismic profiles SY03-THR-Pr01 crossing pockmark A and SY01-THR-Pr02 covering pockmark cluster C. Locations and orientations are shown in Fig. 1. Interpretations from MeBo cores are projected on the seismic lines. High-amplitude reflectors are widespread in the seismic profile.
Figure 8: Schematic representations of the pockmark formation controlled by fluid flow and gas hydrate precipitation during different evolutionary stages (A-E).
Table 1: Basic information of the MeBo cores taken during the Guienco-MeBo cruise as well as upper and lower boundaries of the gas hydrate occurrence zone (GHOZ) estimated using IR thermal scanning and pore water chloride concentration anomalies, respectively. mbsl: meters below sea level. mbsf: meters below seafloor. nd: not detected. nc: not calculated.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Location</th>
<th>Water depth (mbsl)</th>
<th>Core length (m)</th>
<th>Top and base of gas hydrate occurrence in cores (mbsf)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Top Deduced from IR thermal scanning Deduced from chloride profiling Base</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Top Deduced from IR thermal scanning Deduced from chloride profiling Base</td>
</tr>
<tr>
<td>GMMB01&amp;02</td>
<td>NW of pockmark A</td>
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<td>53.30</td>
<td>nd.          nd.</td>
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<tr>
<td>GMMB03</td>
<td>Pockmark A</td>
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<td>45.18</td>
<td>6.9          17.6</td>
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<td>Pockmark A</td>
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<td>6.67</td>
<td>3.1          6.6</td>
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<tr>
<td>GMMB07</td>
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<tr>
<td>GMMB08</td>
<td>Pockmark A</td>
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<td>2.3          26.2</td>
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<tr>
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<td>Pockmark C2</td>
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</tr>
<tr>
<td>GMMB09</td>
<td>SE of Pockmark C2</td>
<td>1196</td>
<td>43.64</td>
<td>38.5         43.6</td>
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</tbody>
</table>
Table 2: Stations of *in situ* sediment temperature measurements in pockmark A with temperatures probes (GMGCT) during the Guineco-MeBo cruise. For calculation of STD, water temperatures measured 50 m above seafloor with the MTLs at individual stations were used. *Note: because of the non-linear slope of the profile this gradient was not considered further.

- **n**: number of probes from which geothermal gradients were calculated.

<table>
<thead>
<tr>
<th>Water depth (m)</th>
<th>Water temperature (°C)</th>
<th>STD (°C)</th>
<th>Thermal gradients (°C/km)</th>
<th><strong>n</strong></th>
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<tbody>
<tr>
<td>GMGCT22</td>
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<td>4.53</td>
<td>0.006</td>
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<tr>
<td>GMGCT23</td>
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<td>GMGCT49</td>
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<td>4.45</td>
<td>0.007</td>
<td>51</td>
</tr>
</tbody>
</table>

*Note: because of the non-linear slope of the profile this gradient was not considered further.*
Center of pockmark A

Periphery of pockmark A

Legend:
- Orange: Sediment without GH
- Blue: Sediment with GH
- Gray: Gas/high CH₄ concentration
- Black: GH presence unclear
- Light blue: GH specific

pockmark C1

pockmark C2

Outside of pockmark C2
Legend
1. Gas hydrate accumulation
2. Gas accumulation below gas hydrate
3. Downward shifting of SMI
4. Dissolution at the top of the gas hydrate
5. Sea floor depression
6. Fracture formation
7. Hummocky sea floor in the center
8. Bubble emission
9. Methane flux in the vicinity of the pockmark
10-12. Repetition of stage A
Highlights:

1. Pockmarks on the Nigerian continental margin were investigated for gas hydrates
2. Long sediment cores were recovered with the portable MeBo drill rig
3. Infrared and pore water chloride measurements revealed gas hydrate distributions
4. Geothermal gradients in the pockmark center up to five fold higher than at the rim
5. Fluid flow and gas hydrate dynamics influence the evolution of pockmarks